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[Title of the Invention] METHOD FOR MANUFACTURING MONOCRYSTALLINE THIN FILM AND MONOCRYSTALLINE THIN FILM DEVICE MANUFACTURED THEREBY

[Technical Field]

[0001]

The present invention relates to a method for manufacturing a high-purity monocrystalline thin film and a monocrystalline thin film device manufactured using the above method.

[Background Art]

[0002]

Hereinafter, conventional methods for manufacturing a monocrystalline silicon thin film will be described.

(a) Oxygen Ion Implantation Method

Oxygen ions are implanted into a monocrystalline silicon substrate, followed by heat treatment, so that a layered structure is formed which is composed of monocrystalline silicon, silicon dioxide, and the monocrystalline silicon substrate.

[0003]

However, when oxygen ions are implanted into the monocrystalline silicon substrate, problems may arise in that many defects are generated in upper-side monocrystalline silicon and the cost of ion implantation is

high (see Patent Document 1 below).

(b) Hydrogen Ion Implantation Method

After hydrogen ions (H+ and H-) are implanted into a monocrystalline silicon substrate, this substrate is adhered to a support substrate, followed by heat treatment. Subsequently, a layer implanted with the hydrogen ions is destroyed and is then peeled away, so that a monocrystalline silicon thin film having a thickness on the order of submicrons can be formed on the support substrate.

[0004]

Since implanted hydrogen can only reach a depth on the order of submicrons, for example, in solar cell applications, the thickness of the monocrystalline silicon thin film must be increased to approximately 10 μm by a chemical vapor deposition or a physical vapor deposition method at a temperature of 1,000°C or more. However, it is difficult to obtain an inexpensive substrate which can satisfy requirements for heat resistance and coefficient of thermal expansion. In addition, a method for increasing the thickness of a monocrystalline silicon thin film before a hydrogen ion implanted layer is peeled away from a substrate cannot be realized since the hydrogen ion implanted layer is destroyed under the film-thickening conditions (see Patent Document 2 below).

(c) Porous Silicon Method

When a surface of a monocrystalline silicon substrate is anodized, fine pores can be formed at a high density. After oxidation treatment is performed on surfaces of the fine pores thus formed, followed by removing parts of oxide layers which are close to the external surface with hydrofluoric acid, annealing is performed in a hydrogen atmosphere. As a result, the top-most surface again forms a continuous monocrystalline film, so that a structure containing a great number of voids is formed thereunder. After this substrate thus treated is adhered to a support substrate, when the layer containing voids is chemically dissolved using a liquid phase method or is mechanically destroyed by water jet or the like, a monocrystalline silicon thin film can be separated (see Patent Document 3 below).

[0005]

However, the thickness of the upper-side silicon film is only approximately 1 μm which is a thickness to be contributed by the surface tension, and when this silicon is used in solar cells, the thickness must be increased by a CVD method. Furthermore, when peeling is performed by mechanical destruction, the monocrystalline silicon substrate is also damaged, and hence a problem may arise in some cases in that the repeated use of the monocrystalline silicon substrate is limited. In addition, a large number

of steps are required, and the process is also disadvantageously complicated.

(d) Melting Recrystallization Method/Melting Crystallization Method

When a silicon dioxide film, a polycrystalline or an amorphous silicon thin film, and a protective layer made of silicon dioxide are laminated in that order on a silicon substrate, and scanning of a line-shaped melting zone by lamp heating or the like is performed, a polycrystalline silicon thin film can be formed in which crystal grains are well grown in the in-plane direction. Subsequently, after the protective layer is chemically dissolved, and the thickness of the polycrystalline silicon thin film is increased by a CVD method, etching of the silicon dioxide film is performed with hydrofluoric acid, so that the polycrystalline silicon thin film can be separated (see Patent Document 4 below).

[0006]

However, since the thin layer thus obtained is merely a polycrystalline silicon thin film, besides inferior energy conversion efficiency, the silicon substrate is also disadvantageously degraded while the molten zone is scanned, and in addition, the process is complicated due to a great number of manufacturing steps.

(e) Epitaxial Lift-Off (ELO) Method Using Sacrificial Layer

Having Different Elemental Composition

This method, previously invented by the inventor of the present invention, is a method comprising the steps of preparing a monocrystalline silicon substrate, forming a sacrificial layer having a different elemental composition and silicon thereon by epitaxial growth, and selectively etching the sacrificial layer, thereby separating an upper-side monocrystalline silicon thin film to reuse the substrate repeatedly (see Patent Document 5 below).

[0007]

However, there is a problem that, in film formation of the upper side monocrystalline silicon thin film by a CVD method, an element of the sacrificial layer is incorporated into the monocrystalline silicon thin film due to diffusion, resulting in inferior energy conversion efficiency. Although the inferior energy conversion efficiency due to the incorporation can be solved by using p-type or n-type highly doped silicon for the sacrificial layer, density distribution of a dopant becomes broad in the vertical direction to the substrate because of the diffusion, so that it has been difficult to perform selective etching in the in-plane direction of the substrate.

[Patent Document 1] Japanese Unexamined Patent Application Publication No. 2000-077352

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 11-040785

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 05-275663

[Patent Document 4] Japanese Unexamined Patent Application Publication No. 07-226528

[Patent Document 5] WO0240751

[Disclosure of Invention]

[Problems to be Solved]

[0008]

The above-described epitaxial lift-off method (e) using a sacrificial layer having a different elemental composition will be further described in detail, and in addition, problems of this method will also be described.

[0009]

Fig. 13 includes cross-sectional views (part 1) showing a process for manufacturing a monocrystalline silicon film by the epitaxial lift-off method described above which uses a sacrificial layer having a different elemental composition.

[0010]

(1) First, a monocrystalline silicon substrate 1 is prepared as shown in Fig. 13(a).

[0011]

(2) Next, as shown in Fig. 13(b), on the surface of the monocrystalline silicon substrate 1, a metal silicide (MSi

x : M indicates a metal in this case) film 2 is epitaxially-grown as an intermediate layer (sacrificial layer).

[0012]

(3) Next, as shown in Fig. 13(c), a monocrystalline silicon film 3 is epitaxially-grown on the surface of the sacrificial layer 2.

[0013]

(4) Subsequently, as shown in Fig. 13(d), the metal silicide film 2 is removed by etching, so that the monocrystalline silicon film 3 is separated.

[0014]

Fig. 14 includes cross-sectional views (part 2) showing a process for manufacturing a monocrystalline silicon film by the epitaxial lift-off method using a sacrificial layer having a different elemental composition.

[0015]

(1) As shown in Fig. 14(a), first of all, a monocrystalline silicon substrate 11 is prepared.

[0016]

(2) Next, as shown in Fig. 14(b), a highly doped silicon film 12 is epitaxially-grown as an intermediate layer (sacrificial layer) on the surface of the monocrystalline silicon substrate 11, or doping is performed onto the surface thereof so as to form an intermediate layer (sacrificial layer).

[0017]

(3) Next, as shown in Fig. 14(c), on the surface of the highly doped silicon film 12, a monocrystalline silicon film 13 is epitaxially-grown.

[0018]

(4) Subsequently, as shown in Fig. 14(d), the highly doped silicon film 12 is removed by etching, so that the monocrystalline silicon film 13 is separated.

[0019]

However, according to the methods for manufacturing a monocrystalline silicon film described above, there have been the following problems.

[0020]

(A) According to the above-described method for manufacturing a monocrystalline silicon film shown in Fig. 13,

when the metal silicide (CoSi2, NiSi2, or CrSi2) film 2 is used as the sacrificial layer, selective etching of this metal silicide film 2 can be easily performed with an aqueous HF solution as an etching agent; however, metal atoms are incorporated into the monocrystalline silicon film 3, and hence a high-purity monocrystalline silicon film cannot be manufactured.

[0021]

(B) According to the above-described method for

manufacturing a monocrystalline silicon film shown in Fig. 14,

when the highly doped silicon film 12 doped with a dopant such as B or P (p-type or n-type can be obtained, respectively, and the resistivity is less than 10-2 Ωcm) is formed as the sacrificial layer, and HF/HNO3/CH3COOH is used as an etching agent, the incorporation of dopant into the monocrystalline silicon film 13 does not cause a problem; however, when the monocrystalline silicon film 13 is epitaxially-grown, the distribution of the dopant becomes very broad because of the diffusion thereof, and as a result, a problem may arise in that the lift-off of the monocrystalline silicon film 13 is not ideally performed.

[0022]

According to the present invention, an object is to provide a method for manufacturing a monocrystalline thin film and a device obtained by using the method mentioned above, the above method being capable to solve the problems described above, to preferably perform the lift-off of the monocrystalline silicon film, and to obtain a high-purity monocrystalline silicon film.

[Means for Solving the Problem]

[0023]

In order to achieve the above described objects, in an epitaxial lift-off method, the present invention uses a

monocrystalline layer containing crystal defects which is formed from the same elemental composition as the sacrificial layer. For example, in manufacturing of a monocrystalline silicon thin film, when silicon is grown on a monocrystalline silicon substrate in an atmosphere containing small amounts of oxygen and water vapor, a silicon layer is being epitaxially-grown as a whole; however, crystal defects such as twins may be included in the silicon layer. Subsequently, when thermal annealing is performed in a reducing atmosphere (hydrogen atmosphere), because of surface diffusion of silicon, defects on the topmost surface are eliminated. When silicon is grown thereon under clean conditions in which crystal defects are not formed, a structure can be formed composed of a monocrystalline silicon thin film/monocrystalline silicon sacrificial layer containing crystal defects/monocrystalline silicon substrate. Since a sacrificial layer containing crystal defects can be selectively etched with a mixed solution containing hydrofluoric acid and an oxidizing agent, the lift-off can be preferably performed, and in addition, a high-purity monocrystalline silicon thin film can be obtained.

[0024]

The method of the present invention would be a high-potential process because it does not lead to the incorporation of elements, which decreases the energy

conversion efficiency, and crystal defects stably exist in bulk and take time to be eliminated. In addition, besides the monocrystalline silicon, the method described above may be applied to manufacturing of a monocrystalline thin film using another optional material, such as Ge, GaAs, GaN, and GeN.

[Effect of the Invention]

[0025]

According to the present invention, the high-purity monocrystalline silicon thin film and device containing a small number of crystal defects can be easily and preferably obtained.

[0026]

By using this monocrystalline silicon thin film as a photovoltaic layer of solar cells, for example, the cost of a solar cell can be significantly reduced.

[0027]

In particular, in a bulk crystal silicon module of which the cost accounts for two thirds of the total cost of a solar-cell power generation system for home use, and in manufacturing of a crystal silicon substrate of which the cost accounts for 40% of the module, the amount of high-purity silicon used for the substrate can be significantly decreased to 1/10 to 1/100.

[0028]

In addition, the apparent problem, that is, shortage of high-purity silicon, can also be solved. Furthermore, when the cost can be reduced to a level competitive to a system power source, the use of solar cells may widely spread without having any political support, and significant expansion of solar cell market can be expected.

[Best Mode for Carrying Out the Invention]

[0029]

Hereinafter, embodiments of the present invention will be described in detail.

[0030]

(1) Fig. 1 includes cross-sectional views (part 1) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[0031]

First, as shown in Fig. 1(a), a monocrystalline substrate 21 is prepared. Next, as shown in Fig. 1(b), a monocrystalline sacrificial layer 22 containing crystal defects is epitaxially-grown using the same material as that of the monocrystalline substrate 21. Then, as shown in Fig. 1(c), a high-purity monocrystalline thin film 23 is epitaxially-grown on this monocrystalline sacrificial layer 22 using the same material as that thereof. Subsequently, as shown in Fig. 1(d), the monocrystalline sacrificial layer 22 is etched (dissolved), and as a result, the high-purity

monocrystalline thin film 23 is manufactured.

[0032]

In addition, the remaining monocrystalline substrate 21 shown in Fig. 1(d) can be reused.

[0033]

(2) Fig. 2 includes cross-sectional views (part 2) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[0034]

First, as shown in Fig. 2(a), a monocrystalline substrate 31 is prepared. Next, as shown in Fig. 2(b), a monocrystalline sacrificial layer 32 containing crystal defects is epitaxially-grown using the same material as that of the monocrystalline substrate 31. Then, as shown in Fig. 2(c), crystal defects on a surface 33 of this monocrystalline sacrificial layer 32 are eliminated. Next, as shown in Fig. 2(d), on the surface 33 of the monocrystalline sacrificial layer 32, the crystal defects of which are eliminated, a high-purity monocrystalline thin film 34 is epitaxially-grown using the same material as that of the monocrystalline sacrificial layer 32. Subsequently, as shown in Fig. 2(e), the monocrystalline sacrificial layer 32 is etched (dissolved), and as a result, the high-purity monocrystalline thin film 34 is manufactured.

[0035]

Also in this case, the remaining monocrystalline substrate 31 shown in Fig. 2(e) can be reused.

[0036]

(3) Fig. 3 includes cross-sectional views (part 3) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[0037]

First, as shown in Fig. 3(a), a monocrystalline substrate 41 is prepared. Next, as shown in Fig. 3(b), a monocrystalline sacrificial layer 42 containing crystal defects is epitaxially-grown using the same material as that of the monocrystalline substrate 41. Then, as shown in Fig. 3(c), a high-purity monocrystalline thin film 43 is epitaxially-grown on this monocrystalline sacrificial layer 42 using the same material as that thereof. Subsequently, as shown in Fig. 3(d), the high-purity monocrystalline thin film 43 is supported by a support base material 44. Next, as shown in Fig. 3(e), the monocrystalline sacrificial layer 42 is etched (dissolved), and as a result, the high-purity monocrystalline thin film 43 supported by the support base material 44 is manufactured.

[0038]

Also in this case, the remaining monocrystalline substrate 41 shown in Fig. 3(e) can be reused.

[0039]

(4) Fig. 4 includes cross-sectional views (part 4) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[0040]

First, as shown in Fig. 4(a), a monocrystalline substrate 51 is prepared. Next, as shown in Fig. 4(b), a monocrystalline sacrificial layer 52 containing crystal defects is epitaxially-grown using the same material as that of the monocrystalline substrate 51. Then, as shown in Fig. 4(c), crystal defects on a surface 53 of this monocrystalline sacrificial layer 52 are eliminated. Next, as shown in Fig. 4(d), on the surface 53 of the monocrystalline sacrificial layer 52, the crystal defects of which are eliminated, a high-purity monocrystalline thin film 54 is epitaxially-grown using the same material as that of the monocrystalline sacrificial layer 52. Subsequently, as shown in Fig. 4(e), the high-purity monocrystalline thin film 54 is supported by a support base material 55. Next, as shown in Fig. 4(f), the monocrystalline sacrificial layer 52 is etched (dissolved), and as a result, the high-purity monocrystalline thin film 54 supported by the support base material 55 is manufactured.

[0041]

Also in this case, the remaining monocrystalline substrate 51 shown in Fig. 4(f) can be reused.

[0042]

(5) In the method for manufacturing a monocrystalline thin film according to one of the above (1) to (4), the monocrystalline substrate is a monocrystalline silicon substrate, the sacrificial layer is a silicon sacrificial layer, and the monocrystalline thin film is a monocrystalline silicon thin film.

[0043]

(6) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), the monocrystalline substrate is a monocrystalline GaAs substrate.

[0044]

(7) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), the monocrystalline substrate is an MgO substrate.

[0045]

(8) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), the step (b) is performed by a physical vapor deposition method or a chemical vapor deposition method at a temperature of 400 to 1,200°C, so that a silicon sacrificial layer containing crystal defects is formed by epitaxial growth.

[0046]

(9) In the method for manufacturing a monocrystalline

thin film, according to one of the above (1) to (4), the crystal defects include twins, vacancies, interstitial atoms, edge dislocations, and screw dislocations.

[0047]

(10) In the method for manufacturing a monocrystalline thin film, according to the above (9), the number density of the crystal defects is 1/μm2 to 1/nm2 at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer.

[0048]

(11) Fig. 5 includes cross-sectional views (part 5) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention. In this case, it is intended to obtain a monocrystalline silicon thin film as the monocrystalline thin film.

[0049]

First, as shown in Fig. 5(a), a monocrystalline silicon substrate 61 is prepared. Next, as shown in Fig. 5(b), under a first film-forming condition in which a remaining gas pressure is relatively high and the temperature is relatively low, silicon is epitaxially-grown to form a monocrystalline silicon sacrificial film 62 containing twins. Next, as shown in Fig. 5(c), by annealing in a reducing atmosphere, twins present on a surface 63 of the monocrystalline silicon sacrificial film 62 are eliminated.

Then, as shown in Fig. 5(d), under a second film-forming condition in which a remaining gas pressure is lower than that under the first film-forming condition and the temperature is high, a monocrystalline silicon thin film 64 containing a small number of defects is epitaxially-grown. Accordingly, as shown in Fig. 5(e), the monocrystalline silicon sacrificial layer 62 is etched (dissolved), and as a result, the high-purity monocrystalline silicon thin film 64 is manufactured.

[0050]

In addition, after being epitaxially-grown, the high-purity monocrystalline silicon film 64 which is supported by a support base material (not shown) may be manufactured by the steps of supporting the monocrystalline silicon film 64, which is located at an upper side, by the support base material and then etching (dissolving) the monocrystalline sacrificial layer 62.

[0051]

Also in this case, the remaining monocrystalline substrate 61 shown in Fig. 5(e) can be reused.

[0052]

(12) In the method for manufacturing a monocrystalline thin film, according to the above (2) or (4), following the step (b), thermal annealing is performed in a reducing atmosphere at a temperature of 1,000 to 1,400°C, so that

crystal defects on the surface of the silicon sacrificial layer are eliminated.

[0053]

(13) In the method for manufacturing a monocrystalline thin film, according to the above (12), after the above annealing, the number density of twins present on the surface of the silicon sacrificial layer is one hundredth or less of that of twins present at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer.

[0054]

(14) In the method for manufacturing a monocrystalline thin film, according to the above (3), the step (c) is performed by a physical vapor deposition method or a chemical vapor deposition method at a temperature of 1,000 to 1,400°C, so that a monocrystalline silicon thin film containing a small number of crystal defects is formed by epitaxial growth.

[0055]

(15) In the method for manufacturing a monocrystalline thin film, according to the above (3), after the monocrystalline silicon thin film is supported by the support base material following the step (c), the silicon sacrificial layer is etched away so as to manufacture a monocrystalline silicon thin film.

[0056]

(16) In the method for manufacturing a monocrystalline thin film, according to the above (3), holes are formed in the monocrystalline silicon substrate at intervals, so that etching of a monocrystalline sacrificial layer is easily performed.

[0057]

(17) In the method for manufacturing a monocrystalline thin film, according to the above (3), the thickness of the silicon sacrificial layer is set to 100 nm or less, so that roughness of the bottom surface of the monocrystalline silicon thin film is reduced to 100 nm or less.

[0058]

(18) In the method for manufacturing a monocrystalline thin film, according to the above (3), the thickness of the silicon sacrificial layer is set to 100 nm or more, so that the bottom surface of the monocrystalline silicon thin film has a texture structure of 100 nm or more.

[0059]

(19) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), a texture structure is formed on the surface of the monocrystalline silicon substrate. Accordingly, in particular, it is intended to improve the energy conversion efficiency when the monocrystalline thin film is used as a

photovoltaic layer of solar cells.

[0060]

(20) In the method for manufacturing a monocrystalline thin film, according to the above (1), (2), (3), or (4), the etching (dissolution) of the monocrystalline sacrificial layer is performed using a mixed solution of hydrofluoric acid and an oxidizing agent.

[0061]

(21) A monocrystalline thin film device is obtained by the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (20).

[0062]

(22) In the monocrystalline thin film device according to the above (21), it is characterized that the monocrystalline thin film is a photovoltaic layer of solar cells.

[0063]

(23) In the monocrystalline thin film device according to the above (21), it is characterized that the monocrystalline thin film is a monocrystalline thin film used for SOI.

[0064]

Hereinafter, particular examples will be described.

[Example 1]

[0065]

Fig. 6 includes cross-sectional views showing manufacturing steps of Example 1 according to the present invention.

[0066]

(1) First, as shown in Fig. 6(a), a monocrystalline silicon substrate (such as 500 μm thick) 71 is prepared.

[0067]

This monocrystalline silicon substrate 71 has a flat upper surface since a monocrystalline silicon sacrificial film, which will be described later, is to be epitaxially-grown.

[0068]

(2) Next, as shown in Fig. 6(b), on the monocrystalline silicon substrate 71, by a sputter-deposition method with substrate heating, silicon containing crystal defects is epitaxially-grown in an atmosphere containing small amounts of oxygen and water vapor. That is, a monocrystalline silicon sacrificial film (such as 0.1 to 1 μm thick) 72 containing crystal defects is formed. This monocrystalline silicon sacrificial film 72 can be easily and precisely removed by etching, as described later.

[0069]

(3) Next, as shown in Fig. 6(c), on the monocrystalline silicon sacrificial film 72, monocrystalline silicon containing a small number of defects is epitaxially-grown by

a CVD method. That is, a high-purity monocrystalline silicon thin film (such as 10 μm thick) 73 containing a small number of crystal defects is formed. Accordingly, a three-layered structure can be formed which is formed of the same material and which includes the monocrystalline silicon sacrificial film 72 containing crystal defects as the intermediate layer.

[0070]

As the epitaxial growth, various methods may be used; for example, as vapor phase growth, a CVD method using a silane gas or a chlorosilane gas or an evaporation method using silicon may be mentioned.

[0071]

(4) Next, as shown in Fig. 6(d), selective etching of the monocrystalline silicon sacrificial film 72 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution, so that the high-purity monocrystalline silicon thin film 73 containing a small number of defects is separated.

[0072]

Fig. 7 is an electron microscope photograph showing a cross-section of a sample which is obtained as described below. The sample is obtained by the steps of forming the silicon sacrificial film 72 containing crystal defects and having a thickness of 0.5 μm on the monocrystalline silicon

substrate 71 by epitaxial growth using a sputter-deposition method with substrate heating at a temperature of 600°C, then forming the monocrystalline silicon thin film 73 containing a small number of defects and having a thickness of 20 μm on the above sacrificial film by a chemical vapor deposition method at a temperature of 1,200°C using a mixture of trichlorosilane and a hydrogen gas as raw materials, and then etching a part of the sacrificial film 72 using a HF/HNO3/CH3COOH mixed solution. In the figure, the state is shown in which the sacrificial film 72 is selectively etched.

[Example 2]

[0073]

Fig. 8 includes cross-sectional views showing manufacturing steps of Example 2 according to the present invention.

[0074]

(1) First, as shown in Fig. 8(a), a monocrystalline silicon substrate (such as 500 μm thick) 81 is prepared.

[0075]

This monocrystalline silicon substrate 81 has a flat upper surface since a monocrystalline silicon sacrificial film, which will be described later, is to be epitaxially-grown.

[0076]

(2) Next, as shown in Fig. 8(b), on the monocrystalline silicon substrate 81, by a sputter-deposition method with substrate heating, silicon containing crystal defects is epitaxially-grown in an atmosphere containing small amounts of oxygen and water vapor. That is, a monocrystalline silicon sacrificial film (such as 0.1 to 1 μm thick) 82 is formed. This monocrystalline silicon sacrificial film 82 can be easily and precisely removed by etching, as described later.

[0077]

(3) Next, as shown in Fig. 8(c), on the monocrystalline silicon sacrificial film 82, monocrystalline silicon containing a small number of defects is epitaxially-grown by a CVD method. That is, a high-purity monocrystalline silicon thin film (such as 10 μm thick) 83 containing a small number of crystal defects is formed. Accordingly, a three-layered structure can be formed which is formed of the same material and which includes the monocrystalline silicon sacrificial film 82 containing crystal defects as the intermediate layer.

[0078]

As the epitaxial growth, various methods may be used; for example, as vapor phase growth, a CVD method using a silane gas or a chlorosilane gas or an evaporation method using silicon may be mentioned.

[0079]

(4) Next, as shown in Fig. 8(d), a support base material 84 is held on the monocrystalline silicon thin film 83. As the support base material 84, a reinforced glass may be used.

[0080]

(5) Next, as shown in Fig. 8(e), selective etching of the monocrystalline silicon sacrificial film 82 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution, so that the high-purity monocrystalline silicon thin film 83 is separated which contains a small number of defects and which is supported by the support base material 84.

[Example 3]

[0081]

Fig. 9 includes cross-sectional views showing manufacturing steps of a monocrystalline thin film of Example 3 according to the present invention.

[0082]

This example is the same as Examples 1 and 2 except that holes 91A are formed in a monocrystalline silicon substrate 91 at intervals. That is,

(1) first, as shown in Fig. 9(a), the monocrystalline silicon substrate 91 is prepared in which the holes 91A are provided at intervals.

[0083]

An optical microscope photograph of a plane surface of the monocrystalline silicon substrate 91 is shown in Fig. 10 in which the holes 91A of 100 μm in diameter are formed at 1 mm intervals by photolithography and selective etching.

[0084]

(2) Next, as shown in Fig. 9(b), on the monocrystalline silicon substrate 91, by a sputter-deposition method with substrate heating, silicon containing defects is epitaxially-grown in an atmosphere containing small amounts of oxygen and water vapor. That is, a monocrystalline silicon sacrificial film 92 is formed.

[0085]

(3) Next, as shown in Fig. 9(c), on the monocrystalline silicon sacrificial film 92, monocrystalline silicon containing a small number of defects is epitaxially-grown by a CVD method. That is, a monocrystalline silicon thin film 93 containing a small number of crystal defects is formed.

[0086]

(4) Next, as shown in Fig. 9(d), a support base material 94 is held on the monocrystalline silicon thin film 93. As the support base material 94, a reinforced glass may be used.

[0087]

(5) Next, as shown in Fig. 9(e), selective etching of

the monocrystalline silicon sacrificial film 92 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution. In this case, since the etchant is likely to enter the holes 91A formed in the monocrystalline silicon substrate 91 at intervals, separation of the monocrystalline silicon thin film 93 having a small number of defects can be smoothly performed. That is, the monocrystalline silicon sacrificial film 92 can be rapidly and precisely removed.

[0088]

In this example, the formation of holes is applied to the manufacturing method of Example 2 and may also be applied to that of Example 1.

[0089]

In addition, by decreasing the thickness of the silicon sacrificial layer 92 to 100 nm or less, the roughness of the bottom surface of the monocrystalline silicon thin film 93 can be reduced to 100 nm or less.

[0090]

Alternatively, by increasing the thickness of the silicon sacrificial layer 92 to 100 nm or more, a texture structure of 100 nm or more may be formed on the bottom surface of the monocrystalline silicon thin film 93. In particular, when the monocrystalline silicon thin film is used as a photovoltaic layer of solar cells, sunlight can be efficiently brought into the monocrystalline thin film, and

hence the energy conversion efficiency can be improved.

[Example 4]

[0091]

Fig. 11 includes cross-sectional views showing manufacturing steps of a monocrystalline thin film of Example 4 according to the present invention.

[0092]

This example is the same as Examples 1 and 2 except that a texture structure 101A is formed on the surface of a monocrystalline silicon substrate 101. That is,

(1) first, as shown in Fig. 11(a), the monocrystalline silicon substrate 101 having the texture structure 101A formed on the surface thereof is prepared.

[0093]

The rate of dissolution of the {111} plane of silicon by an alkali solution is slowest. An electron microscope photograph of a cross-section of the substrate 101 is shown in Fig. 12 which is formed of a Si(100) wafer and a pyramid-shaped texture of the {111} planes provided thereon by using the properties described above.

[0094]

(2) Next, as shown in Fig. 11(b), on the monocrystalline silicon substrate 101 thus prepared, by a sputter-deposition method with substrate heating, silicon containing defects is epitaxially-grown in an atmosphere

containing small amounts of oxygen and water vapor. That is, a monocrystalline silicon sacrificial film 102 having the texture structure 102A on the surface thereof is formed.

[0095]

(3) Next, as shown in Fig. 11(c), on the monocrystalline silicon sacrificial film 102, monocrystalline silicon containing a small number of defects is epitaxially-grown by a CVD method. That is, a monocrystalline silicon thin film 103 containing a small number of crystal defects is formed which has a texture structure 103B on the front surface and a texture structure 103A on the rear surface.

[0096]

(4) Next, as shown in Fig. 11(d), a support base material 104 is held on the monocrystalline silicon thin film 103.

[0097]

(5) Next, as shown in Fig. 11(e), selective etching of the monocrystalline silicon sacrificial film 102 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution, so that the monocrystalline silicon thin film 103 is separated which is supported by the support base material 104 and which has the texture structure 103A on the front surface and the texture structure 103B on the rear surface.

[0098]

In this example, the formation of a texture structure is applied to the manufacturing method of Example 2 and may also be applied to that of Example 1.

[0099]

In addition, with the configuration as described above, particularly, when a monocrystalline silicon thin film containing a particularly small number of defects is used as a photovoltaic layer of solar cells, the energy conversion efficiency can be improved.

[0100]

By the method described above, a monocrystalline silicon thin film containing a small number of defects or a monocrystalline silicon thin film which contains a small number of defects and which is supported by a support base material can be obtained and can then be used for a monocrystalline thin film device. For example, the above monocrystalline silicon thin film can be used as a photovoltaic layer of solar cells or can be used for an SOI (Silicon On Insulator) semiconductor device.

[0101]

In particular, in the case in which a monocrystalline silicon thin film having a texture structure thereon is used, when it is used as a photovoltaic layer of solar cells, solar light can be efficiently brought into the

monocrystalline thin film, and hence the energy conversion efficiency can be improved.

[0102]

The present invention is not limited to the examples described above, and various modifications may be performed without departing from the spirit and the scope of the present invention and may not be excluded therefrom.

[Industrial Applicability]

[0103]

The present invention is suitably applied, for example, to methods for manufacturing photovoltaic layers of solar cells and monocrystalline thin films of silicon and compound semiconductors used for semiconductor devices and to methods for manufacturing SOI substrates.

[Brief Description of the Drawings]

[0104]

[Fig. 1] Cross-sectional views (part 1) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 2] Cross-sectional views (part 2) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 3] Cross-sectional views (part 3) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 4] Cross-sectional views (part 4) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 5] Cross-sectional views (part 5) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 6] Cross-sectional views showing manufacturing steps of Example 1 according to the present invention.

[Fig. 7] An electron microscope photograph showing a cross-section of a sample which is obtained when a part of a sacrificial layer of Example 1 according to the present invention is etched.

[Fig. 8] Cross-sectional views showing manufacturing steps of Example 2 according to the present invention.

[Fig. 9] Cross-sectional views showing manufacturing steps of a monocrystalline thin film of Example 3 according to the present invention.

[Fig. 10] An optical microscope photograph showing a plane surface of a substrate provided with holes of Example 3 according to the present invention.

[Fig. 11] Cross-sectional views showing manufacturing steps of a monocrystalline thin film of Example 4 according to the present invention.

[Fig. 12] An electron microscope photograph showing a cross-section of a substrate having a pyramid-shaped texture

of Example 4 according to the present invention.

[Fig. 13] Cross-sectional views (part 1) showing manufacturing steps of a monocrystalline silicon film by a conventional epitaxial lift-off method using a sacrificial layer having a different elemental composition.

[Fig. 14] Cross-sectional views (part 2) showing manufacturing steps of a monocrystalline silicon film by a conventional epitaxial lift-off method using a sacrificial layer having a different elemental composition.

[Description of Symbols]

[0105]

21, 31, 41, 51: monocrystalline substrate

22, 32, 42, 52: monocrystalline sacrificial layer

23, 34, 43, 54: high-purity monocrystalline thin film

33, 53: surface of monocrystalline sacrificial layer

44, 55, 84, 94, 104: support base material

61, 71, 81, 91, 101: monocrystalline silicon substrate

62, 72, 82, 92, 102: monocrystalline silicon sacrificial film

63: surface of monocrystalline silicon sacrificial film

64, 73, 83, 93, 103: monocrystalline silicon thin film

91A: hole

101A, 102A, 103A, 103B: texture structure

[Name of Document] DRAWINGS

[Fig. 1]

[Fig. 2]

[Fig. 3]

[Fig. 4]

[Fig. 5]

[Fig. 6]

[Fig. 7]

[Fig. 8]

[Fig. 9]

[Fig. 10]

[Fig. 11]

[Fig. 12]

[Name of Document] CLAIMS

[Claim 1] A method for manufacturing a monocrystalline thin film, comprising the steps of;

(a) preparing a monocrystalline substrate;

(b) forming a sacrificial layer containing crystal defects on the monocrystalline substrate using the same material by epitaxial growth;

(c) forming a monocrystalline thin film containing crystal defects on the sacrificial layer using the same material by epitaxial growth, the number of the crystal defects being smaller than that of the sacrificial layer; and

(d) etching the sacrificial layer so as to form a monocrystalline thin film containing a small number of crystal defects.

[Claim 2] The method for manufacturing a monocrystalline thin film, according to Claim 1, further comprising the step of eliminating crystal defects present on the surface of the sacrificial layer following the step (b).

[Claim 3] The method for manufacturing a monocrystalline thin film, according to Claim 1 or 2, wherein the monocrystalline substrate is a monocrystalline silicon substrate, the sacrificial layer is a silicon sacrificial layer, and the monocrystalline thin film is a

monocrystalline silicon thin film.

[Claim 4] The method for manufacturing a monocrystalline thin film, according to Claim 1 or 2, wherein the monocrystalline substrate is a monocrystalline GaAs substrate.

[Claim 5] The method for manufacturing a monocrystalline thin film, according to Claim 1 or 2, wherein the monocrystalline substrate is a monocrystalline MgO substrate.

[Claim 6] The method for manufacturing a monocrystalline thin film, according to Claim 3, wherein the step (b) is performed by a physical vapor deposition method or a chemical vapor deposition method at a temperature of 400 to 1,200°C, whereby a silicon sacrificial layer containing crystal defects is epitaxially-grown.

[Claim 7] The method for manufacturing a monocrystalline thin film, according to Claims 3 or 6, wherein the crystal defects include twins, vacancies, interstitial atoms, edge displacements, and screw displacements.

[Claim 8] The method for manufacturing a monocrystalline thin film, according to one of Claims 3, 6, and 7, wherein the number density of the crystal defects is 1/μm2 to 1/nm2 at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer.

[Claim 9] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 8, wherein twins exist at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer at a number density of 1/μm2 to 1/nm2.

[Claim 10] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 9, further comprising, following the step (b), the step of performing thermal annealing in a reducing atmosphere at a temperature of 1,000 to 1,400°C to eliminate crystal defects on the surface of the silicon sacrificial layer.

[Claim 11] The method for manufacturing a monocrystalline thin film, according to Claim 10, wherein after the thermal annealing, the number density of twins present on the surface of the silicon sacrificial layer is one hundredth or less of that of twins present at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer.

[Claim 12] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 11, wherein the step (c) is performed by a physical vapor deposition method or a chemical vapor deposition method at a temperature of 1,000 to 1,400°C, whereby the monocrystalline silicon thin film containing a small number of crystal defects is formed by epitaxial growth.

[Claim 13] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 12, further comprising, following the step (c), the steps of: supporting the monocrystalline silicon thin film by a support base material, and then etching the silicon sacrificial layer so as to manufacture the monocrystalline silicon thin film.

[Claim 14] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 13, further comprising the step of forming holes in the monocrystalline silicon substrate at intervals.

[Claim 15] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 14, wherein the thickness of the silicon sacrificial layer is set to 100 nm or less so that roughness of the bottom surface of the monocrystalline silicon thin film is reduced to 100 nm or less.

[Claim 16] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 14, wherein the thickness of the silicon sacrificial layer is set to 100 nm or more so that the bottom surface of the monocrystalline silicon thin film has a texture structure of 100 nm or more.

[Claim 17] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and

6 to 16, further comprising the step of forming a texture structure on the surface of the monocrystalline silicon substrate.

[Claim 18] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 17, wherein the etching of the silicon sacrificial layer is performed using a mixed solution of hydrofluoric acid and an oxidizing agent.

[Claim 19] A monocrystalline thin film device obtained by the method for manufacturing a monocrystalline thin film, according to one of Claims 1 to 5.

[Claim 20] A monocrystalline thin film device obtained by the method for manufacturing a monocrystalline silicon thin film, according to one of Claims 3 and 6 to 18.

[Claim 21] The monocrystalline thin film device according to Claim 20, wherein the monocrystalline silicon thin film is a photovoltaic layer of solar-cells.

[Claim 22] The monocrystalline thin film device according to Claim 20, wherein the monocrystalline silicon thin film is a monocrystalline silicon thin film used for SOI.

[Name of Document] ABSTRACT

[Abstract]

[Object] The present invention provides a method for manufacturing a monocrystalline film and a device formed by the above method, and according to the method mentioned above, lift-off of the monocrystalline silicon film is preferably performed and a high-purity monocrystalline silicon film can be obtained.

[Solving Means] A monocrystalline silicon substrate (template Si substrate) 201 is prepared, and on this monocrystalline silicon substrate 201, an epitaxial sacrificial layer 202 is formed. Subsequently, on this sacrificial layer 202, a monocrystalline silicon thin film 203 is rapidly epitaxially-grown using a RVD method, followed by etching of the sacrificial layer 202, whereby a monocrystalline silicon thin film 204 used as a photovoltaic layer of solar cells is formed.

[Selected Drawing] Fig. 6